

Letter

Protection of polymer from atomic-oxygen erosion using Al₂O₃ atomic layer deposition coatingsRussell Cooper^a, Hari P. Upadhyaya^a, Timothy K. Minton^{a,*}, Michael R. Berman^b,
Xiaohua Du^c, Steven M. George^c^a Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, USA^b Air Force Office of Scientific Research, 875 N. Randolph Street, Arlington, VA 22203, USA^c Departments of Chemistry and Biochemistry and Chemical and Biological Engineering, University of Colorado, Boulder, CO 80309, USA

Received 8 April 2007; received in revised form 2 July 2007; accepted 13 July 2007

Available online 21 July 2007

Abstract

Thin films of Al₂O₃ grown using atomic layer deposition (ALD) techniques can protect polymers from erosion by oxygen atoms. To quantify this protection, polyimide substrates with the same chemical repeat unit as Kapton[®] were applied to quartz crystal microbalance (QCM) sensors. Al₂O₃ ALD films with varying thicknesses were grown on the polyimide substrates. The ALD-coated polyimide materials were then exposed to a hyperthermal atomic-oxygen beam. The mass loss versus oxygen-atom exposure time was measured *in situ* by the QCM. Al₂O₃ ALD film thicknesses of ~35 Å were found to protect the polymer from erosion.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Polymers; Polyimide; Atomic layer deposition; Al₂O₃; Atomic oxygen; Erosion; Quartz crystal microbalance

Spacecraft in low Earth orbit collide with ambient oxygen atoms with relative velocities of ~7.4 km s⁻¹ and fluxes in the range of 10¹³ to 10¹⁵ atoms cm⁻² s⁻¹. These high-energy collisions cause oxidation and erosion of materials. Organic polymers used on the external surfaces of spacecraft as structural and thermal-control materials are particularly vulnerable to atomic oxygen [1–4]. Coatings of inorganic oxides, such as SiO₂, have been used to provide protection from atomic oxygen. These coatings are generally applied by plasma enhanced chemical vapor deposition (PECVD).

PECVD is known to produce films that tend to be columnar with a large defect density. Because of the large number of defects, relatively thick coatings have been used to reduce the defect density. Kapton[®] polyimide surfaces that have SiO₂ coatings with a 1300 Å thickness have been shown to exhibit erosion yields as low as ~0.1–0.2% of the erosion yield of unprotected Kapton[®] [5,6].

However, handling and thermal cycling of these thick coatings are likely to produce cracks in the coatings and expose the substrate to potential O-atom attack. Atomic oxygen that reaches the substrate through defects may erode large cavities underneath the coating in the vicinity of the defect [6,7].

The PECVD coating technique also requires line-of-sight to the substrate. This requirement may be impractical for shadowed or high-aspect-ratio structures. An approach that is an improvement over PECVD is to attach silicon-containing moieties to the surface through a photochemical reaction. The modified surface may then react with atomic oxygen to form a continuous layer of SiO₂. Although this technique has demonstrated a one hundred-fold reduction in erosion yield for flat samples, there are still line-of-sight limitations when the technique is applied to non-planar surfaces [8].

In addition to protecting existing polymers with inorganic coatings, inorganic/organic copolymers are being developed that take advantage of the reaction of the inorganic component with atomic oxygen to form a passivating oxide layer. This protection strategy has the advantage that the oxide layer can reform after the degradation of the initial oxide layer. An earlier

* Corresponding author.

E-mail addresses: tminton@montana.edu (T.K. Minton),
Michael.Berman@afosr.af.mil (M.R. Berman), Steven.George@colorado.edu
(S.M. George).

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 02 JUL 2007		2. REPORT TYPE		3. DATES COVERED 00-00-2007 to 00-00-2007	
4. TITLE AND SUBTITLE Protection of polymer from atomic-oxygen erosion using Al2O3 atomic layer deposition coatings				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO, 80309				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT see report					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 4	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

class of self-passivating polymers was based on phosphine oxide [9]. More recently, copolymers that include polyoligo-meric silsesquioxane have shown great promise as a replacement for Kapton® [10]. However, these polymers exhibit finite erosion by atomic oxygen and may experience damage under vacuum ultraviolet (VUV) radiation in space.

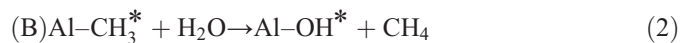
Earlier studies indicate that an ultrathin and flexible inorganic oxide coating may provide an effective barrier. Exposure of a silicon surface to a beam of hyperthermal atomic oxygen leads to the growth of an SiO₂ film with a terminal thickness of ~50 Å [11–13]. The native thickness of aluminum oxide (Al₂O₃) on aluminum has also been measured to be only 30–40 Å [14]. Anecdotal evidence from space flight experiments exists that an Al₂O₃ coating with a nominal thickness of 50 Å protects a reactive substrate [15]. If such thin and flexible oxide coatings can be applied to polymer substrates without line-of-sight restrictions and without defects, then they should be able to protect the substrate even after handling and thermal cycling.

Chemical vapor deposition (CVD) is a well characterized thin film deposition method that does not depend on line-of-sight. However, CVD methods typically require elevated substrate temperatures to grow the desired films. A variation on CVD is atomic layer deposition (ALD). ALD can usually employ more reactive precursor gases than CVD and achieve lower deposition temperatures. ALD techniques can also produce continuous, Angstrom-level-controlled, and defect-free films [16]. ALD is a gas-phase method based on two sequential, self-limiting surface reactions [17]. Each surface reaction allows only ~1 monolayer of deposition.

Al₂O₃ ALD is a particularly robust and well-defined ALD system [18,19]. Al₂O₃ ALD films can be pinhole-free as demonstrated by electrical measurements [20], and they can be deposited on polymer substrates [21,22]. Excellent gas diffusion barrier properties are observed for Al₂O₃ ALD films on polyethylene naphthalate (PEN) and Kapton® polymer substrates [23,24]. Consequently, Al₂O₃ ALD should provide an ideal model system for the systematic investigation of thin-film coatings to protect a polymer from hyperthermal atomic oxygen.

Quartz crystal microbalance (QCM) sensors were used to study the efficacy of thin Al₂O₃ ALD films to protect a polymer. Polyimide substrates were prepared on 0.5-inch-diameter QCM disc sensors. The precursor to the polyimide was Pyralin® PI5878G from HD Microsystems. This polyamic acid as purchased was dissolved in 1-methyl-2-pyrrolidinone. The polyamic acid was diluted and then spin-coated onto gold-coated QCM sensors. Before spin-coating, the QCM sensors were modified by applying an adhesion promoter (HD Microsystems VM651) and heating the substrates in an air oven to 80 °C to remove any residual water. After spin-coating, the samples were allowed to dry in air under a watch glass for two days. The samples were then placed in a vacuum furnace (Centurion VPM) and cured with the following schedule: 2 h at 50 °C, 2 h at 80 °C, 1 h at 200 °C, and 2 h at 270 °C. The chemical repeat unit of the resulting polyimide is equivalent to that of DuPont Kapton®. The polyimide layers on the QCM disc sensors were determined by profilometry to have thicknesses in the range of 800–1000 nm.

Aluminum oxide (Al₂O₃) ALD coatings with various thicknesses were applied to the polyimide substrates using sequential, self-limiting exposures to trimethylaluminum (TMA) (Aldrich) and water (Fisher HPLC-grade). The Al₂O₃ ALD was performed at 177 °C in a viscous flow, hot-wall ALD flow reactor [25]. The TMA and H₂O yield Al₂O₃ ALD according to the following two reactions [18,19]:



where the asterisks denote the surface species. When performed in an ABAB... reaction sequence, these sequential reactions produce linear, atomic-layer-controlled Al₂O₃ growth. The steady-state Al₂O₃ ALD growth rate after nucleation is ~1.2 Å per AB cycle [19,26]. The polyimide substrates were coated with Al₂O₃ ALD films resulting from 8, 13, 17, 21, 25 and 50 AB cycles, respectively. The reactant exposure sequence was TMA (1.0 s), purge (20 s), H₂O (1.0 s), and purge (10 s). The polyimide surfaces were coated without any prior surface treatment or functionalization.

The coated QCM sensors were exposed to a beam containing hyperthermal atomic oxygen. Mass loss was measured *in situ* versus time using a Maxtek QCM head (Model DSH-200) and a Model RQCM data collection system. The QCM head accommodated two discs, allowing each atomic-oxygen exposure to be conducted with an Al₂O₃-coated polyimide test sample and a polyimide control sample without an Al₂O₃ coating. For each exposure, the atomic-oxygen flux was determined from the mass-loss rate of the polyimide control sample. The oxygen-atom flux did not vary by more than a few percent from one exposure to another. Test and control samples were always placed in the same locations to ensure consistency between the various exposures.

A pictorial diagram of the atomic-oxygen source and experimental apparatus is shown in Fig. 1. This apparatus has

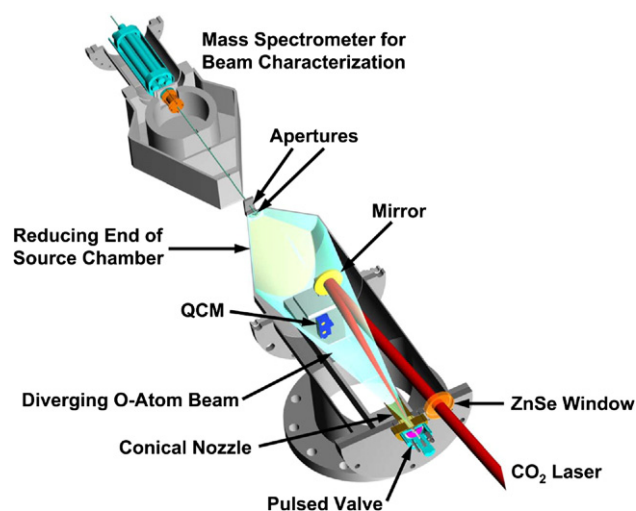


Fig. 1. Experimental apparatus used to measure the mass loss of spin-coated polyimide layers on QCM sensors during exposure to a hyperthermal atomic-oxygen beam.

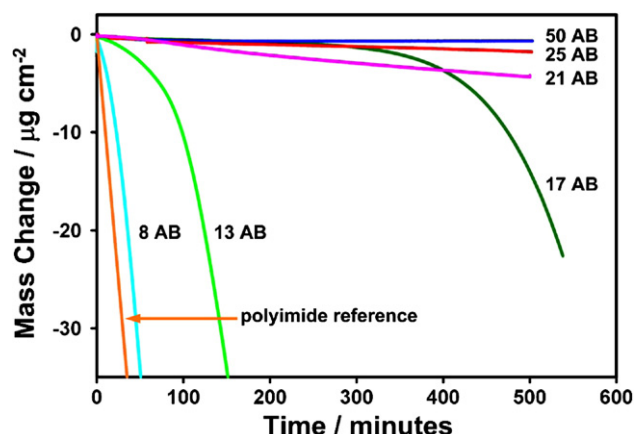


Fig. 2. Mass change of polyimide substrates coated with varying numbers of Al_2O_3 ALD AB cycles versus exposure time to atomic oxygen.

been described in detail previously [1,10,27,28]. Sample exposures were performed with a pulsed beam operating at a repetition rate of 2 Hz. The pulsed beam contained hyperthermal $\text{O}(^3P)$ atoms and O_2 molecules that were generated with a laser-breakdown source [28,29]. Average translational energies for atomic and molecular oxygen were ~ 5.4 and ~ 9.3 eV, respectively. The energy widths (full width at half maximum) of the atomic and molecular oxygen components were ~ 2.0 and ~ 5.3 eV, respectively. The average mole fraction of atomic oxygen in the beam was $\sim 90\%$.

The hyperthermal O-atom beam was directed at the polymer samples on QCM sensors that were positioned about 40 cm from the apex of the conical nozzle. Mass loss as a function of time for both the test and control samples was recorded for at least 500 min. This time corresponds to 60,000 pulses of the hyperthermal beam for each atomic-oxygen exposure. Based on the erosion yield of a Kapton[®] H polyimide [27], the atomic-oxygen flux was $\sim 2 \times 10^{15}$ O atoms cm^{-2} pulse $^{-1}$.

Mass loss results for Al_2O_3 ALD film thicknesses resulting from 8, 13, 17, 21, 25 and 50 AB cycles are shown in Fig. 2. The uncoated polyimide control sample eroded away completely during every experiment. The linear mass loss rate for the control sample was consistent with a loss of $600 \mu\text{g cm}^{-2}$ after 500 min. Polyimide samples with Al_2O_3 ALD films after 8 and 13 AB cycles eroded before 500 min of exposure. The sample with an Al_2O_3 ALD film after 17 AB cycles showed a rapid change of slope after 300 min of exposure and probably would have eroded completely if the exposure had significantly exceeded 500 min.

The samples with Al_2O_3 ALD films after 21 and 25 AB cycles showed a very gradual loss of mass during the exposure. The mass loss for the sample after 25 AB cycles is only slightly higher than the mass loss expected when oxygen atoms remove residual contamination from the surface. The polyimide sample coated with an Al_2O_3 ALD film after 50 AB cycles did not exhibit any measurable mass change after more than 500 min of exposure. This Al_2O_3 ALD film presumably has no defects or pinholes where O atoms could attack the polyimide substrate. The measurements suggest a threshold of ≥ 25 AB cycles for Al_2O_3 ALD coatings to protect a polymer substrate from erosion by oxygen atoms with ~ 5 eV of translational energy.

The erosion of polymer substrates by an oxygen plasma in the vicinity of coating defects has previously been used to make defects more visible to SEM and optical inspection [30]. Defects in the ALD coatings would be expected to be similarly amplified by exposure to the hyperthermal O-atom beam. Scanning electron microscope (SEM) images of the exposed surfaces showed erosion that was consistent with the mass loss measurements. The SEM images also demonstrated the sensitivity of the QCM to identify mass loss from erosion at tiny defects on the surface.

Fig. 3 shows SEM images for exposed surfaces with Al_2O_3 ALD films after 17, 21 and 50 AB cycles for atomic oxygen exposure times of 500 min. The left and right columns consist of images collected with low ($\times 20$) and high ($\times 1000$) magnification, respectively. The number and size of defects decrease as the number of AB cycles increases. The surface after 17 AB cycles exhibits numerous large round defects that appear as regions where the polymer substrate has eroded significantly. The surface after 21 AB cycles has many small defects scattered over the surface. The surface after 50 AB cycles does not show any defects that can be related to the atomic-oxygen exposure.

The Al_2O_3 ALD films after 8, 13, 17 and 21 AB cycles are poor protecting barriers against attack by oxygen atoms. Earlier QCM and X-ray fluorescence measurements revealed that approximately 10–20 AB cycles are required to nucleate a continuous Al_2O_3 film on various polymer substrates [22,31]. Prior to nucleation, the ALD reactants are observed by QCM measurements to absorb into the polymer [22]. After nucleation, an Al_2O_3 ALD film barrier continuously covers the polymer and blocks any reactant absorption into the polymer.

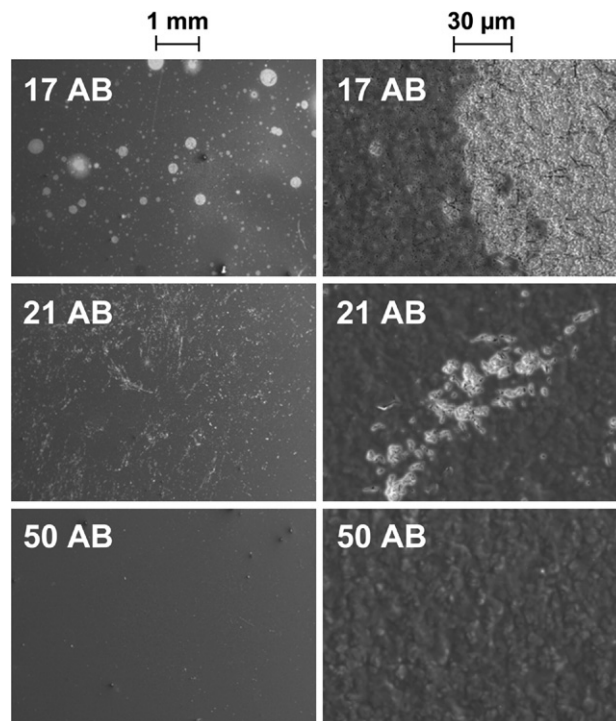


Fig. 3. SEM images of polyimide substrates coated with 17, 21, and 50 Al_2O_3 ALD AB cycles after exposure to atomic oxygen. The left and right columns display images collected with $\times 20$ and $\times 1000$ magnification, respectively.

The absence of defects on the polyimide sample after 50 AB cycles of Al_2O_3 ALD is consistent with the observation of no mass loss during atomic-oxygen exposure. This Al_2O_3 ALD film is an excellent protecting layer for the polyimide substrate. The thin Al_2O_3 ALD film after 50 AB cycles should have an Al_2O_3 ALD film thickness on top of the polymer surface of ~ 35 Å. This estimated thickness assumes that the Al_2O_3 ALD film requires 20 AB cycles to nucleate on the polyimide substrate [22, 31].

The Al_2O_3 ALD thickness of ~ 35 Å required to protect the polyimide can be compared with the native oxide thickness of 30–40 Å on aluminum nanoparticles [14]. This native oxide thickness serves as barrier to prevent additional aluminum oxidation. Earlier measurements of the water vapor transmission rate through Al_2O_3 ALD films on PEN and Kapton[®] also measured extremely low transmission rates for Al_2O_3 ALD film thicknesses >50 Å [24]. The H_2O permeability is believed to be dominated by defects [32]. Analogous behavior may be occurring for atomic oxygen penetration through the Al_2O_3 ALD films.

Comparison of the Al_2O_3 ALD thickness of ~ 35 Å with the SiO_2 film thickness of ~ 50 Å formed by oxidation of silicon in a hyperthermal atomic oxygen beam [11–13] suggests that Al_2O_3 is more effective at blocking hyperthermal O atoms. Al_2O_3 ALD films can be deposited on polymers of any geometry. The Al_2O_3 ALD films should also remain flexible and uncompromised if the polymer is bent during handling or if the polymer expands and contracts during thermal cycling. The Al_2O_3 ALD films with a thickness of 35 Å were deposited with 50 AB cycles with each cycle requiring approximately 32 s. The time required to deposit this film could be shortened considerably with the use of an optimized reactor design. The ALD method may also be used to apply oxide coatings other than Al_2O_3 . Multilayer ALD films of $\text{Al}_2\text{O}_3/\text{TiO}_2$ or $\text{Al}_2\text{O}_3/\text{ZnO}$ could protect against both O atoms and VUV light.

Acknowledgement

This work was supported by the Air Force Office of Scientific Research (FA9550-04-1-0428 and FA9550-06-1-0075).

References

- [1] T.K. Minton, D.J. Garton, in: R.A. Dressler (Ed.), *Chemical Dynamics in Extreme Environments*, Advanced Series in Physical Chemistry, vol. 11, World Scientific, Singapore, 2001, p. 420.
- [2] E. Murad, J. Spacecr. Rockets 33 (1996) 131.
- [3] L.E. Murr, W.H. Kinard, Am. Sci. 81 (1993) 152.
- [4] R.C. Tennyson, Can. J. Phys. 69 (1991) 1190.
- [5] S.K. Rutledge, J.A. Mihelic, in: V. Srinivasan, B.A. Banks (Eds.), *Materials Degradation in Low Earth Orbit (LEO)*, The Minerals, Metals & Materials Society, 1990, p. 35.
- [6] S.K. Rutledge, R.M. Olle, 38th International SAMPE Symposium, May 10–13, 1993 Covina, CA, Int. SAMPE Symp. Exhib., vol. 38, 1993, p. 679.
- [7] B.A. Banks, A. Snyder, S.K. Miller, K.K. de Groh, R. Demko, J. Spacecr. Rockets 41 (2004) 335.
- [8] J.I. Kleiman, Mater. Res. Soc. Symp. Proc. 851 (2005) 343.
- [9] J.W. Connell, J.G. Smith, J.L. Hendrick, Polymer 36 (1995) 13.
- [10] A.L. Brunsvold, T.K. Minton, I. Gouzman, E. Grossman, R. Gonzalez, High Perform. Polym. 16 (2004) 303.
- [11] M. Tagawa, T. Ema, H. Kinoshita, N. Ohmae, M. Umeno, T.K. Minton, Jpn. J. Appl. Phys., Part 2 37 (1988) L1455.
- [12] M. Tagawa, K. Yokota, N. Ohmae, H. Kinoshita, High Perform. Polym. 12 (2000) 53.
- [13] M. Kisa, T.K. Minton, J.C. Yang, J. Appl. Phys. 97 (2005) 023520.
- [14] C.E. Aumann, G.L. Skofronick, J.A. Martin, J. Vac. Sci. Technol., B 13 (1995) 1178.
- [15] S.Y. Chung, D.E. Brinza, T.K. Minton, A.E. Stiegman, J.T. Kenny, R.H. Liang, JPL Publication 93-91 (Prepared for the Ballistic Defense Organization by the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA., 1993).
- [16] T. Suntola, Thin Solid Films 216 (1992) 84.
- [17] S.M. George, A.W. Ott, J.W. Klaus, J. Phys. Chem. 100 (1996) 13121.
- [18] A.C. Dillon, A.W. Ott, J.D. Way, S.M. George, Surf. Sci. 322 (1995) 230.
- [19] A.W. Ott, J.W. Klaus, J.M. Johnson, S.M. George, Thin Solid Films 292 (1997) 135.
- [20] M.D. Groner, J.W. Elam, F.H. Fabreguette, S.M. George, Thin Solid Films 413 (2002) 186.
- [21] J.D. Ferguson, A.W. Weimer, S.M. George, Chem. Mater. 16 (2004) 5602.
- [22] C.A. Wilson, R.K. Grubbs, S.M. George, Chem. Mater. 17 (2005) 5625.
- [23] P.F. Carcia, R.S. McLean, M.H. Reilly, M.D. Groner, S.M. George, Appl. Phys. Lett. 89 (2006) 031915.
- [24] M.D. Groner, S.M. George, R.S. McLean, P.F. Carcia, Appl. Phys. Lett. 88 (2006) 051907.
- [25] J.W. Elam, M.D. Groner, S.M. George, Rev. Sci. Instrum. 73 (2002) 2981.
- [26] M.D. Groner, F.H. Fabreguette, J.W. Elam, S.M. George, Chem. Mater. 16 (2004) 639.
- [27] D.M. Buczala, A.L. Brunsvold, T.K. Minton, J. Spacecr. Rockets 43 (2006) 421.
- [28] D.J. Garton, A.L. Brunsvold, T.K. Minton, D. Troya, B. Maiti, G.C. Schatz, J. Phys. Chem., A 110 (2006) 1327.
- [29] G.E. Caledonia, R.H. Krech, B.D. Green, AIAA J. 25 (1987) 59.
- [30] A.S. da Silva Sobrinho, G. Czeremuszkin, M. Latrèche, G. Dennler, M.R. Wertheimer, Surf. Coat. Technol. 116–119 (1999) 1204.
- [31] J.W. Elam, C.A. Wilson, M. Schuisky, Z.A. Sechrist, S.M. George, J. Vac. Sci. Technol., B 21 (2003) 1099.
- [32] G.L. Graff, R.E. Williford, P.E. Burrows, J. Appl. Phys. 96 (2004) 1840.